Overlap Integrals of Interatomically Orthogonal 2s, 2p - Hybrid Orbitals

Sigeru NAGAHARA

Overlap integrals S of interatomically orthogonal 2s, 2p—hybrid orbitals are formulated in convenient form and computed and tabulated as a function of the hybridization coefficient (angle parameter α) and the interatomic distance parameter $\rho=\delta R$ for the case of two like first row atoms.

§ 1. Introduction

As is well known, the quantity known as the overlap integral is of considerable importance in the theory of molecular structure. Although the existing literature[1] contains a number of formulas and some numerical values for any desired type of hybrid can be obtained very easily from the tables as simple linear combinations of non-hybrid overlap integral values, it is thought worth while to carry out the numerical study for hybrid AO's in convenient form, whose results are presented below.

§ 2. Intratomically Orthogonal AO's Sets

In general, we construct the intratomically orthogonal 2s, 2p—hybrid AO's in homopolar bonds (see Fig. 1~5, Table 1~4).

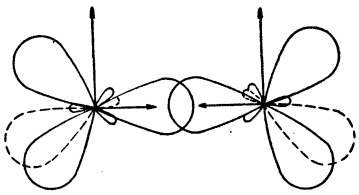


Fig. 1
The tetrahedrally hybridized bonding in ethane molecul in the case of $\alpha=\tan^{-1}\frac{1}{\sqrt{8}}$

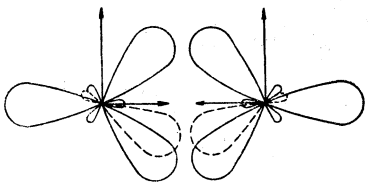
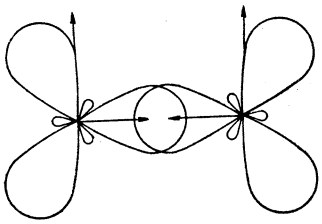


Fig. 2
The tetrahedrally hybridized bonding in acetylene molecule in the case of $\alpha=\tan^{-1}\frac{1}{\sqrt{8}}$



The π—orbitals of the two atoms are not shown to avoid confusion. They are directed perpendicularly to the plane of the paper.

Fig. 3
The trigonally hybridized bonding in the ethylene molecule in the case of $\alpha=30°$(trigonal sp^2 hybridization model)

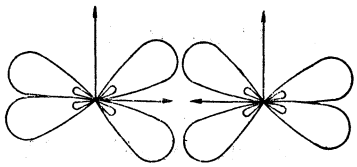
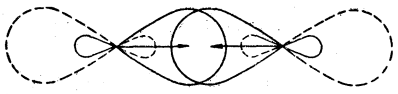


Fig. 4
The tetrahedrally hybridized bonding in ethylene molecule in the case of $\alpha=\beta=\tan^{-1}\frac{1}{\sqrt{2}}$



The four π−orbitals of the two atoms are not shown. They are in perpendicular pairs at right angles to the line of the two atoms.

Fig. 5
The π−model in acetylene molecule

Model Ⅰ and Model Ⅱ :

$$\varphi_1=\frac{1}{N}(as+\cos\alpha.x\mp\sin\alpha.z)$$

$$\varphi_2=\frac{1}{N}(as-\frac{1}{2}\cos\alpha\ x-\sin\frac{\varphi}{2}y\mp\sin\alpha.z)$$

$$\varphi_3=\frac{1}{N}(as-\frac{1}{2}\cos\alpha\ x+\sin\frac{\varphi}{2}y\pm\sin\alpha.z)$$

$$\varphi_4=\frac{1}{N_4}(a_4s\mp z)$$

where

$$N_1=1+a_1,\ N_4^2=1+a_4^2$$

$$\sin^2\frac{\varphi}{2}=\frac{3}{4}\cos^2\alpha$$

$$a^2=\frac{3}{2}\cos^2\alpha-1$$

$$a_4a=\sin\alpha$$

special case (tetrahedrally hybridized bonding in ethane)

$$\frac{\varphi_0}{2}=90°-35°.25$$

$$\cos^2\alpha_0=\frac{8}{9},\ \sin^2\alpha_0=\frac{8}{9}$$

$$a^2=a_4^2=\frac{1}{3}$$

$$N^2=N_4^2=\frac{4}{3}$$

upper sign for model Ⅰ, lower sign for model Ⅱ

Table 1

Model Ⅲ :

$$\varphi_1=\frac{1}{N}(as+\cos\alpha\ x-\sin\alpha\ z)$$

$$\varphi_2=\frac{1}{N}(as-\cos\alpha\ x-\sin\alpha.z)$$

$$\varphi_3=y$$

$$\varphi_4=\frac{1}{N_4}(a_4s+z)$$

where

$$N^2=2\cos^2\alpha,\ N_4^2=\cos^2\alpha/\cos2\alpha$$

$$a^2=\cos2\alpha$$

$a_4 a = \sin\alpha$

special case (trigonal sp^2hyridization in ethylene)

$\alpha = 30°$

$a^2 = a_4^2 = \frac{1}{2}$

$N^2 = N_4^2 = \frac{3}{2}$

Table 2

Model Ⅳ :

$$\varphi_1 = \frac{1}{N}(as + \cos\alpha x - \sin\alpha z)$$

$$\varphi_2 = \frac{1}{N}(as - \cos\alpha x - \sin\alpha z)$$

$$\varphi_3 = \frac{1}{N'}(a's + \cos\beta y + \sin\beta z)$$

$$\varphi_4 = \frac{1}{N'}(a's - \cos\beta y + \sin\beta z)$$

where

$N^2 = 2\cos^2\alpha$, $N'^2 = 2\cos^2\beta$

$a^2 = \cos 2\alpha$, $a'^2 = \cos 2\beta$

$aa' = \sin\alpha\sin\beta$

special case (tetrahedrally hybridized bonding in ethylene)

$\alpha = \beta = 35°25$ $\tan^2\alpha = \tan^2\beta = \frac{1}{2}$

$a^2 = a'^2 = \frac{1}{3}$

$N^2 = N'^2 = \frac{4}{3}$

Table 3

Model Ⅴ :

$\varphi_1 = x$

$\varphi_2 = y$

$$\varphi_3 = \frac{1}{N_3}(as - z)$$

$$\varphi_4 = \frac{1}{N_4}(a's + z)$$

where

$N_3^2 = 1 + a^2$, $N_4^2 = 1 + a'^2$

$aa' = 1$ $(a = \tan\alpha')$

specialcase

$a = a' = 1$ $\alpha' = 45°$

$N_3 = N_4 = \sqrt{2}$

Table 4

System Ⅰ and system Ⅱ represent the tetrahedrally hybridized bonding[2] in ethane

molecule and acetylene molecule in the case of $\alpha=\tan^{-1}\frac{1}{\sqrt{8}}$, system Ⅲ shows the trigonally hybridized bonding in the ethylene molecule as superposition of a σ bond formed by overlaps of two unhybridized p-type orbitals in the case of $\alpha=30°$ (trigonal sp^2 hybridization system), system Ⅳ shows the tetrahedrally hybridized bonding in ethylene molecule in the case of $\alpha=\beta=\tan^{-1}\frac{1}{\sqrt{2}}$ in which the carbon atoms are hybridized tetrahedrally and linked together by the pairing of two sets (φ_3, φ_4), $(\varphi_{3'}, \varphi_{4'})$ of orbitals[3] and system Ⅴ is the π-model in acetylene molecule which is composed of one σ and two π-bonds and here also the π-bonds are formed between electrons in non-hybridized p status. The σ electrons, two to each carbon atom, are located in sp hybridized orbitals, formed by the linear combination of one s and one p wave function and the molecule is therefore linear.

The AO's are adopted as follows[4] :

$$\left.\begin{aligned}
&(2s)=(\delta^5/3\pi)^{\frac{1}{2}}\exp(-\delta\gamma_{a_1})\gamma_{a_1}\\
&(2p\sigma)=(\delta^5/\pi)^{\frac{1}{2}}\exp(-\delta\gamma_{a_1})\gamma_{a_1}\cos\theta_{a_1}\\
&(2p\pi)=(\delta^5/\pi)^{\frac{1}{2}}\exp(-\delta\gamma_{a_1})\gamma_{a_1}\sin\theta_{a_1}\cos\varphi\\
&(2p\pi')=(\delta^5/\pi)^{\frac{1}{2}}\exp(-\delta\gamma_{a_1})\sin\theta_{a_1}\sin\varphi
\end{aligned}\right\}\quad\cdots\cdots\cdots\cdots(1)$$

where (2s), (2pσ), ····· are the atomic orbitals. In the above, the coordinate system is chosen as follows : the position of the electron is denoted by P, $\gamma_{a_1}=\overline{AP}$, $\gamma_{b_1}=\overline{BP}$, $\alpha_{a_1}=\angle BAP$, $\theta_{b_1}=\angle ABP$

§ 3. Overlap Integrals for 2s, 2p-hybrid AO's in Homopolar Bonds

We consider the overlap integral $S(\varphi_i \varphi_{j'})=S_{ij'}$ for two like 2s, 2p-hybrid AO's (see Table 1~4) of two like atoms.

In terms of the overlap integrals $S_{ss'}$, $S_{s\sigma'}$ and $S_{\sigma\sigma'}$ for pure 2s, pure 2pσ and pure 2s—2pσ AOs', these formulation which are obtained in convenient form by the author, are shown in Table 5~9.

Model Ⅰ :

$$\begin{aligned}
S_{11'}&=S_{22'}=S_{33'}\\
&=\frac{1}{3}S_{ss'}+\frac{2}{3}S_{xx'}+\frac{2}{3}\tan^2\alpha(S_{zz'}-S_{ss'})-\frac{2}{3}\sqrt{6}\,v\tan\alpha S_{sz'}\\
S_{44'}&=S_{zz'}+2\tan^2\alpha(S_{ss'}-S_{zz'})+2\sqrt{6}\,v\tan\alpha S_{sz'}\\
S_{12'}&=S_{13'}=S_{23'}\\
&=\frac{1}{3}S_{ss'}-\frac{1}{3}S_{xx'}+\frac{2}{3}\tan^2\alpha(S_{zz'}-S_{ss'})-\frac{2}{3}\sqrt{6}\,v\tan\alpha S_{sz'}\\
S_{14'}&=S_{24'}=S_{34'}\\
&=\sqrt{2}\,v\tan\alpha(S_{ss'}-S_{zz'})+\frac{1}{\sqrt{3}}(1-2\tan^2\alpha)S_{sz'}-\frac{2}{\sqrt{3}}\tan^2\alpha S_{sz'}
\end{aligned}$$

where

$$v=\left(\cos^2\alpha-\frac{2}{3}\right)^{\frac{1}{2}}/\cos\alpha$$

Table 5

Madel Ⅱ :

$$S_{11}'=S_{22}'=S_{33}'$$
$$=\frac{1}{3}S_{ss'}+\frac{2}{3}S_{xx'}+\frac{2}{3}\tan^2\alpha(S_{zz'}-S_{ss'})+\frac{2\sqrt{6}}{3}v\tan\alpha S_{sz'}$$
$$S_{44}'=S_{zz'}+2\tan^2\alpha(S_{sz'}-S_{zz'})-2\sqrt{6}\,v\tan\alpha S_{sz'}$$
$$SS_{12}'=S_{13}'=S_{23}'$$
$$=\frac{1}{3}S_{ss'}-\frac{1}{3}S_{xx'}+\frac{2}{3}\tan^2\alpha(S_{zz'}-S_{ss'})+\frac{2\sqrt{6}}{3}v\tan\alpha S_{sz'}$$
$$S_{14}'=S_{24}'=S_{34}'$$
$$=\sqrt{2}\,v\tan\alpha(S_{ss'}-S_{zz'})-\frac{1}{\sqrt{3}}(1-2\tan^2\alpha)S_{zs'}+\frac{2}{\sqrt{3}}\tan^2\alpha S_{sz'}$$

where

$$v=\left(\cos^2\alpha-\frac{2}{3}\right)^{\frac{1}{2}}/\cos\alpha$$

Table 6

Model Ⅲ :

$$S_{11}'=S_{zz'}$$
$$=\frac{1}{2}S_{ss'}+\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\alpha(S_{zz'}-S_{ss'})-w\tan\alpha S_{sz'}$$
$$S_{44}'=S_{zz'}+\tan^2\alpha(S_{ss'}-S_{zz'})+2w\tan\alpha S_{sz'}$$
$$S_{12}'=\frac{1}{2}S_{ss'}-\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\alpha(S_{zz'}-S_{ss'})-w\tan\alpha S_{sz'}$$
$$S_{14}'=S_{24}'$$
$$=\frac{1}{\sqrt{2}}S_{sz'}-\sqrt{2}\tan^2\alpha S_{sz'}+\frac{1}{\sqrt{2}}w\tan\alpha(S_{ss'}-S_{zz'})$$

where

$$w=(\cos2\alpha)^{\frac{1}{2}}/\cos\alpha$$

Table 7

Model Ⅳ :

$$S_{11}'=S_{zz'}$$
$$=\frac{1}{2}S_{ss'}+\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\alpha(S_{zz'}-S_{ss'})-\tan\alpha\tan\beta S_{sz'}$$
$$S_{33}'=S_{44}'$$
$$=\frac{1}{2}S_{ss'}+\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\beta(S_{zz'}-S_{ss'})+\tan\alpha\tan\beta S_{sz'}$$
$$S_{12}'=\frac{1}{2}S_{ss'}-\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\alpha(S_{zz'}-S_{ss'})-\tan\alpha\tan\beta S_{sz'}$$
$$S_{34}'=\frac{1}{2}S_{ss'}-\frac{1}{2}S_{xx'}+\frac{1}{2}\tan^2\beta(S_{zz'}-S_{ss'})+\tan\alpha\tan\beta S_{sz'}$$
$$S_{13}'=S_{14}'=S_{23}'=S_{24}'$$
$$=\frac{1}{2}S_{sz'}-\tan^2\alpha S_{sz'}+\frac{1}{2}\tan\alpha\tan\beta(S_{ss'}-S_{zz'})$$

where

$$\tan^2\alpha+\tan^2\beta=1$$

Table 8

Model Ⅴ :

$$S_{33}' = \sin^2\alpha' S_{ss'} - 2\sin\alpha'\cos\alpha' S_{sz'} + \cos^2\alpha' S_{zz'}$$

$$S_{44}' = \cos^2\alpha' S_{ss'} + 2\sin\alpha'\cos\alpha' S_{sz'} + \sin^2\alpha' S_{zz'}$$

$$S_{34}' = \sin\alpha'\cos\alpha'(S_{ss'} - S_{zz'}) + (\sin^2\alpha' - \cos^2\alpha') S_{sz'}$$

where

$$\alpha = \tan\alpha'$$

Table 9

The values of $S(\varphi_{i'}\varphi_{j'}) = S_{i'j'}$ depend on α (parameter relating for bonding angle) and on a parameter $\rho = \delta R$ proportional to the internuclear distance R.

Using the values of M. Kotani's Table[5] for $S_{ss'}$, $S_{s\sigma'}$ and $S_{\sigma\sigma'}$, we carry out the numerical evaluation for $S_{i'j'}$, variating α and ρ. A part of these result are shown in Table 10.

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Model Ⅰ : (tetrahedrally hybridized bonding in ethane)

ρ	2.00	2.50	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
S_{11}'	0.51427	0.42183	0.33787	0.2951	0.2606	0.2291	0.2006	0.1749	0.1518	0.1313	0.1132	0.0974
S_{12}'	−0.18045	−0.15663	−0.13013	−0.1226	−0.1095	−0.0975	−0.0863	−0.0760	−0.0667	−0.0583	−0.0507	−0.0438
S_{14}'	0.43526	0.32982	0.23568	0.1932	0.1590	0.1274	0.1007	0.0792	0.0604	0.0450	0.0323	0.0222
S_{44}'	0.43608	0.56449	0.71488	0.7591	0.7679	0.7631	0.7468	0.7213	0.6886	0.6509	0.6093	0.5653

Model Ⅱ : (tetrahedrally hybridized bonding in acetylene)

S_{44}'	−0.33690	−0.30767	−0.16181	−0.1241	−0.0901	−0.0613	−0.0368	−0.0173	+0.0014	0.0107	0.0201	0.0265
S_{12}'	0.08721	0.13454	0.16361	0.1722	0.1765	0.1773	0.1749	0.1702	0.1633	0.1551	0.1457	0.1358
S_{14}'	0.16760	0.03911	−0.05655	−0.0785	−0.1056	−0.1261	−0.1402	−0.1481	−0.1519	−0.1519	−0.1490	−0.1437
S_{11}'	0.78193	0.71255	0.63161	0.5895	0.5466	0.5039	0.4618	0.4211	0.3818	0.3447	0.3096	0.2770

Model Ⅲ : (trigonal sp^2 hybridization in ethylene)

S_{11}'	0.36291	0.29380	0.23304	0.2064	0.1818	0.1594	0.1394	0.1214	0.1053	0.0912	0.0785	0.0675
S_{12}'	−0.33181	−0.28420	−0.23004	−0.2110	−0.1884	−0.1673	−0.1476	−0.1296	−0.1132	−0.0985	−0.0855	−0.0738
S_{14}'	0.45613	0.36342	0.27945	0.2418	0.2079	0.1775	0.1505	0.1269	0.1062	0.0884	0.0738	0.0603
S_{44}'	0.55835	0.71263	0.79869	0.8145	0.8162	0.8051	0.7831	0.7524	0.7151	0.6726	0.6283	0.5814

Mobel Ⅳ : (teterahedrally hybridized bonding in ethylene)

S_{11}'	0.26293	0.21821	0.17875	0.1630	0.1465	0.1303	0.1160	0.1029	0.0909	0.0802	0.0704	0.0616
S_{12}'	−0.43179	−0.35980	−0.28925	−0.2535	−0.2242	−0.1964	−0.1711	−0.1481	−0.1276	−0.1095	−0.0939	−0.0797
S_{13}'	0.26015	0.18354	0.11948	0.0976	0.0746	0.0550	0.0386	0.0251	0.0143	0.0057	−0.0009	−0.0059
S_{34}'	0.03181	0.14374	0.21953	0.2458	0.2616	0.2704	0.2729	0.2701	0.2632	0.2529	0.2320	0.2083
S_{44}'	0.72653	0.72175	0.68753	0.6632	0.6315	0.5971	0.5599	0.5211	0.4817	0.4426	0.4040	0.3668

Model Ⅴ : (π−model in acetylene, $\alpha=\alpha'=1$, $\alpha'=45°$)

S_{34}'	0.52029	0.36710	0.23898	0.18583	0.1400	0.10114	0.0688	0.0423	0.0211	0.00447	−0.00825	−0.01762
S_{44}'	0.75838	0.86550	0.90707	0.90542	0.89098	0.86571	0.83161	0.79067	0.74476	0.69557	0.64459	0.59310
S_{33}'	−0.16883	−0.14156	−0.11048	−0.09542	−0.08128	−0.06831	−0.05665	−0.04636	−0.03740	−0.02971	−0.02321	−0.01778

Table 10